Effect of Polyacid Architecture and Polycation Molecular Weight on Lateral Diffusion within Multilayer Films

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ABSTRACT

Despite the potential use of polyelectrolyte multilayers for biomedical, separation, and energy applications, their dynamic properties are not sufficiently understood. In this work, center-of-mass diffusion of a weak polyacid – poly(methacrylic acid) (PMAA) of linear and 8-arm architecture

(*L*-PMAA and 8-PMAA, respectively) and matched molecular weight – was studied in layer-by-layer (LbL) assemblies with poly(diallyldimethylammonium) chloride (PDADMAC) of varied molecular weight. The film deposition at low-salt, acidic conditions when PMAA was only partially ionized yielded thicker, more diffused layers with shorter PDADMAC chains, and bilayer thickness decreased for multilayers constructed with longer PDADMAC. The molecular architecture of PMAA had a weak effect on film growth, with bilayer thickness being ~20% larger for *L*-PMAA for the films constructed with the shortest PDADMAC (35 kDa), and identical film growth for *L*-PMAA and 8-PMAA with the longest PDADMAC (300 kDa). Exposure of the multilayer films to 0.2 M NaCl triggered a reduction in PMAA ionization and significant lateral diffusivity of fluorescently labeled PMAA molecules (PMAA*), with diffusion coefficients D ranging from 10^{-13} to 10^{-12} cm^2/s, as determined by the fluorescence recovery after photobleaching (FRAP) technique. For all the films, polymer mobility was higher for star polyacids as compared to their linear counterparts, and the dependence of PMAA diffusion coefficient D on PDADMAC molecular weight ($D \sim M^{-n}$) was relatively weak ($n<0.6$). However, 8-PMAA demonstrated an approximately doubled power exponent compared to the *L*-PMAA chains, suggesting a stronger effect of molecular connectivity of the partner polycation molecules on diffusion of star polyelectrolytes.

Introduction

Ultrathin coatings constructed via the layer-by-layer (LbL) deposition technique are widely used in photonics, energy storage, biomedical engineering, and drug delivery applications.[1-5] In most cases, the application conditions for these coatings are different from the assembly conditions. Thus, it is essential to understand how environmental stimuli, such as changes in salt

concentrations, temperatures and/or pHs, affect the behavior of the LbL films. Multilayer assemblies exposed to different environments can swell/deswell,[6,7] alter their surface morphologies[8-11] or even disassemble.[12-16] All these events require macromolecular adjustments on the polymer chain and segments *via* polymer chain dynamics, adjustment of polymer conformation and/or number of ionic contacts between assembled polyelectrolytes, affecting the chain mobility within the polymer coatings. An important fundamental question which was addressed in only a few experimental studies involving linear polyelectrolytes is the molecular weight (MW) dependence of the mobility of assembled polymer chains.

Previously, our group has explored this question using the fluorescence recovery after photobleaching (FRAP) technique with LbL systems containing fluorescently labeled chains of linear poly(methacrylic acid) (PMAA) of different MWs. These prior studies demonstrated that the lateral diffusion coefficient (D) scaled with the PMAA MW as $D \sim M_w^{-1\pm0.05}$, suggesting the persistence of the unentangled polymer dynamics to a PMAA MW as high as 480 kDa.[17] Significant contribution to studies of molecular mobility of polyelectrolytes within LbL films by Helm's group explored the diffusion of a strong, fully charged polyanion, poly(styrene sulfonate) (PSS), in the direction perpendicular to the film surface using neutron reflectometry (NR). Helm's work highlighted the interdependence of molecular conformations determined by the assembly conditions, post-annealing salt concentrations, and MW of a partner polymer, poly(diallyldimethylammonium) chloride (PDADMAC), on PSS mobility.[18,19] Importantly, the PDADMAC MW was the main factor affecting the diffusion coefficient of PSS (D_{PSS}) with D_{PSS} not following the power law dependences predicted by the reptation model for polymer melts (*i.e.,* $D \propto M_w^{-2}$ by theoretical predictions, and $D \propto M_w^{-2.3}$ as determined experimentally).[20,21] Specifically, for largely mismatched MWs of PSS and PDADMAC (*i.e.,* larger number of repeat

units in PDADMAC), D_{PSS} dramatically dropped with the power law, exceeding the reptation prediction, with the power exponent dependent on the conformation of assembled polyelectrolytes.[19] These studies suggested a possible role of PDADMAC 'entanglements', or the diffusion landscape which is determined by the spatial distribution of ionic pairs, on PSS diffusion and proposed coupling between PDADMAC and PSS diffusion. While the prior works provided the insight of a MW dependence on the diffusion of polyelectrolytes within multilayer assemblies, they were limited only to linear chains, and similar dependences remained unexplored for branched polyelectrolytes.

Our previous work regarding polymer dynamics in star-containing LbL films demonstrated enhanced diffusivity of linear chains in the star-containing films[22,23] and an increased size of the polymer segments that participate in the diffusion of star polymers.[23] The aim of this work is to explore how the MW of PDADMAC affects the lateral diffusion of a star polyanion – 8-PMAA – and compare it to its linear counterpart, *L*-PMAA. Unlike prior work that explored a similar question for a linear strong polyanion (PSS), we use a weak polyelectrolyte (PMAA) whose charge density is affected by solution pH and hypothesize that both the reduced charge density in acidic conditions and intrinsically weaker binding of PMAA to polycations (as compared to PSS)[24] can decouple the mobility of the polyanion from that of PDADMAC. We employed the FRAP technique to directly track the diffusion of linear and star PMAA and establish the correlation between the mobility of polymers of varied architecture with the MW dependence of the polycation. Our findings indicate that the effect of MW of PDADMAC on polyacid diffusion was weaker than sticky Rouse or sticky reptation theoretical predictions[25] for associating polymers.

Results and Discussion

Growth and salt stability of PMAA/PDADMAC LbL films

To explore the effect of polycation MW on polymer dynamics of linear and star polyacids within multilayer films, we assembled up to 10 bilayers of PDADMAC of different MWs (35 kDa, 75 kDa and 300 kDa) with *L*-PMAA and 8-PMAA of matched MW (M_w ~ 60 kDa) via LbL assembly from solutions at pH 5 (0.2 mg/mL in 0.01 M phosphate buffer, 5 min each layer). Figure 1 shows that the MW of PDADMAC strongly impacts the growth of all-linear and star-containing LbL films. Specifically, films containing 35 kDa PDADMAC demonstrated ~2.2-fold larger bilayer thickness in the linear regime compared with films constructed with 300 kDa PDADMAC. This effect is likely related to faster chain mobility of the low-MW PDADMAC during deposition. Note that while the average thickness of individual PMAA layers measured by ellipsometry during film construction remained ~3-5 nm for all the films, the thickness of individual PDADMAC layers decreased from ~15 nm to 2-3 nm when the PDADMAC MW decreased from 35 kDa to 300 kDa (Fig. S1). This behavior is likely due to the selected film assembly conditions (pH 5), which, according to the prior study of linear poly(acrylic acid)/PDADMAC films, corresponds to the regime in which film growth is dominated by the diffusivity of PDADMAC chains during film deposition.[26] The slightly higher bilayer thicknesses in the *L*-PMAA-containing (as compared to 8-PMAA-containing) films is distinct from the previously reported faster growth of star-containing films in a different LbL system in which growth was dominated by the faster diffusion of star PMAA.[22,23] The observed differences are also likely attributed to higher chain rigidity and the reduced charge density of PDADMAC (see Fig. S2), twice lower than that of earlier explored poly[2-(dimethylamino)ethyl methacrylate].

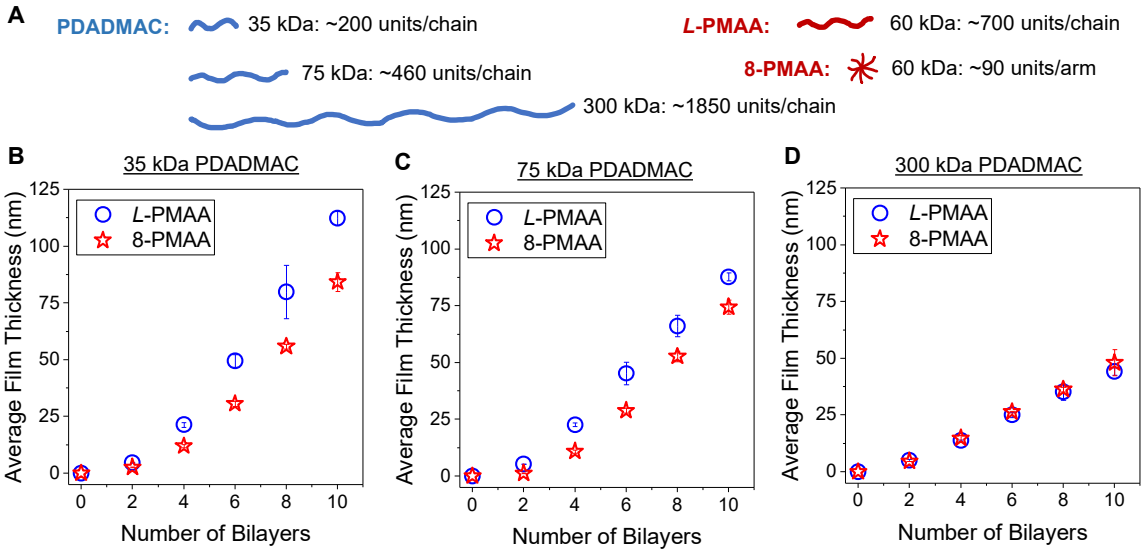

Figure 1. Schematics showing the proportional lengths of the PDADMAC and PMAA molecules (A), and growth curves of linear (blue circles) and 8-arm (red stars) PMAA assembled with 35 kDa (B), 75 kDa (C), and 300 kDa (D) PDADMAC, as determined by spectroscopic ellipsometry. LbL films were deposited from solutions at pH 5 (0.2 mg/mL in 0.01 M phosphate buffer, 5 minutes each layer).

Next, we studied the stability of the coatings upon exposure to increasing NaCl concentrations. Fig. 2A-C shows that an increase in PDADMAC MW led to enhanced stability of the films, in agreement with the stronger interpolymer interactions indicated by the growth curves. Temporal studies of the *L*-PMAA and 8-PMAA LbL systems upon exposure to 0.2 M NaCl showed stability after about 50 minutes (Fig. S3). For all systems, star-containing films were more prone to deconstruction by salt ions compared to their linear counterparts, suggesting that the star architecture slightly hinders ionic pairing between the weak polyacid and PDADMAC. For the films containing 35 kDa and 75 kDa PDADMAC, this is corroborated by ionization of assembled PMAA analyzed *via* transmission FTIR of thick films (100-250 nm; Figs. 2D, E and S4), which showed lower ionization of assembled 8-PMAA molecules.

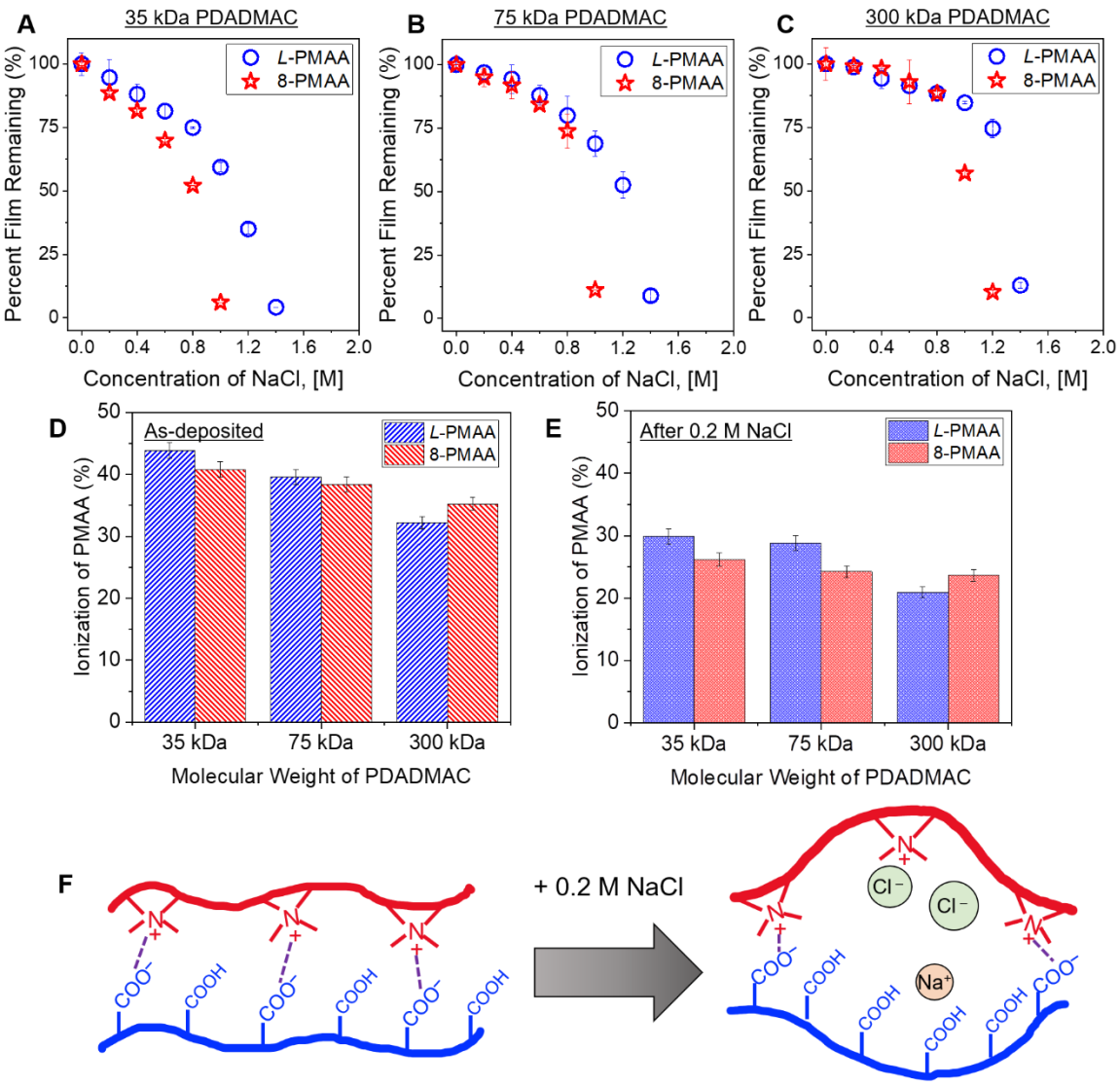

Figure 2. Salt stability of 10-bilayer linear (blue circles) and 8-arm (red stars) PMAA assembled with (A) 35 kDa, (B) 75 kDa, and (C) 300 kDa PDADMAC, as determined by spectroscopic ellipsometry. Percent ionization of carboxylic acid groups in PMAA in *L*-PMAA/PDADMAC (blue) and 8-PMAA/PDADMAC (red) films before (D) and after (E) exposure to 0.2 M NaCl for 10 minutes. Screening by salt ions is represented schematically in panel F.

Figs. 2D&E also show that for both linear and star-containing films, PMAA ionization consistently decreased with the increase of PDADMAC MW, suggesting that longer PDADMAC chains are less successful in conforming to their shorter counterparts, probably due to their more sluggish dynamics. However, one of the most pronounced trends seen in Fig. 2D&E is a 10-15% decrease in PMAA ionization upon the exposure of the film to 0.2 M NaCl. The drop in ionization

is due to the inclusion of salt ions within LbL films, disruption of polymer-polymer ionic pairs, and the resultant protonation of the released carboxylic groups, as shown in Fig. 2F. The effect is enabled by the stronger impact of a polycation[27] as compared to low-molecular salt[28,29] on ionization of weak polyacids. The inclusion of salt within LbL films could be detected by *in situ* measurements of film swelling using spectroscopic ellipsometry, showing increased swelling of all films upon exposure to salt solution, with all 8-PMAA-containing films swelling more upon salt exposure than their linear counterparts (Fig. S5).

Lateral diffusion of polyacids in LbL films

We further explored the lateral diffusion ($D_{//}$) of the linear and star polyacids assembled with PDADMAC of different MWs. To enable $D_{//}$ measurements with FRAP, the linear and 8-arm PMAAs were fluorescently labeled with Alexa-488 with one label per 800-1,000 PMAA units as reported previously and denoted as PMAA*.[23] Fluorescent correlation spectroscopy (FCS) was used to study attachment of Alexa-488 to the polymer chains by measuring the diffusion of polyacids and free labels in solutions. FCS measurements of fluorescently labeled *L*-PMAA*, 8-PMAA*, and control Alexa-488 in solution at pH 5 confirmed covalent attachment of the fluorescent labels to the polymer chains (Fig. S6). The auto-correlation function of *L*-PMAA* and 8-PMAA* showed monodisperse model fitting (meaning all label was attached to the polymer chains, and no label is free in the polymer solutions), yielding diffusion coefficient values of 37.6 $\mu m^2/s$ and 36.1 $\mu m^2/s$, respectively for *L*-PMAA* and 8-PMAA*. For the multilayer films used in FRAP experiments, the following design of $(PDADMAC/PMAA)_3/(PDADMAC/PMAA^*)_4/(PDADMAC/PMAA)_3$ was used in which labeled PMAA was deposited within the middle of the film to avoid any effects of the film/substrate and film/solution interfaces. Because our selected conditions for FRAP were in 0.2 M NaCl solutions

at pH 5.0, all films were exposed to the selected conditions overnight prior to FRAP measurements to complete minor salt-induced film thickness changes (3 to 18% depending on the film composition, Fig. S3). Fig. S3 shows that the minor loss of film thicknesses equilibrated after 50 minutes of exposure to salt, so that no film thickness loss occurred during FRAP experiments, which were initiated after 12 hours of film pre-conditioning in 0.2 M NaCl. Further details of the experiments are described in the Materials and Methods section of Supporting Information. Figure 3 shows fluorescence recovery curves for linear (Fig. 3A) and star (Fig. 3B) PMAAs. For all systems, complete fluorescence recovery was not achieved which could be a result of partial crosslinking of polymer chains during photobleaching.[30] The recovery data was fitted using an exponential fit, given by the equation: $I = I_{eq} + Ae^{\frac{-t}{\tau}}$ where I_{eq} defines equilibrium intensity, I is intensity at time t, A is the amplitude, and τ is recovery time. The half time was determined when 50% of the total intensity recovery was achieved, and was calculated as $t_{1/2} = \tau \ln(2)$. The lateral diffusion coefficients were calculated from the half time using the following equation: $D_{//} = \frac{yR^2}{4t_{1/2}}$ where y is the constant beam shape factor (value: 0.88), R is the bleaching spot size (0.33 μm) and $t_{1/2}$ is the half time.[23]

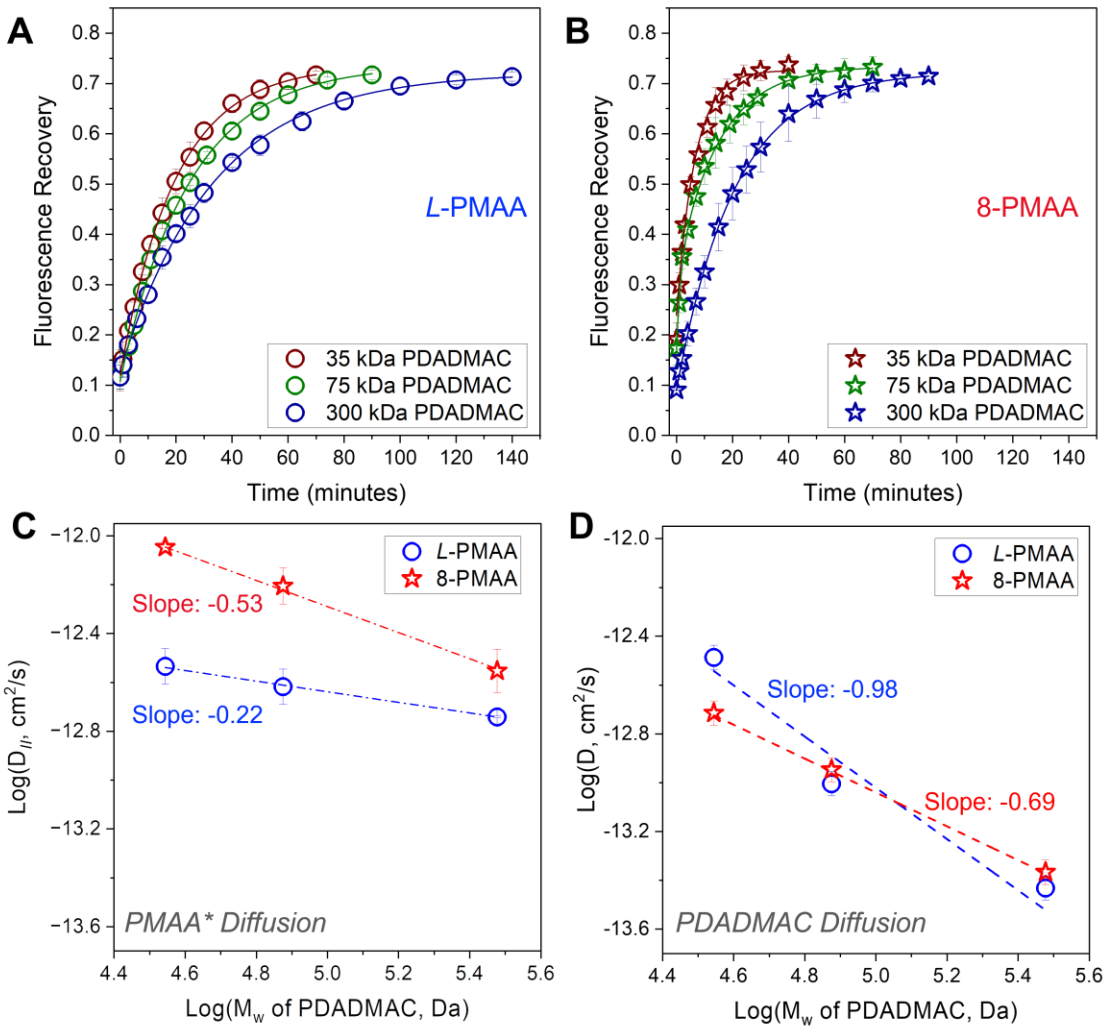

Figure 3. FRAP recovery curves for diffusion of fluorescently labeled polyacids in (*L*-PMAA/PDADMAC)$_3$(*L*-PMAA*/PDADMAC)$_4$(*L*-PMAA/PDADMAC)$_3$ (A) and (8-PMAA/PDADMAC)$_3$(8-PMAA*/PDADMAC)$_4$(8-PMAA/PDADMAC)$_3$ (B) films in 0.2 M NaCl at pH 5. (C) Effect of PDADMAC MW on lateral diffusion coefficients of *L*-PMAA/PDADMAC (blue) and 8-PMAA/PDADMAC (red) films. (D) Effect of PDADMAC MW on perpendicular diffusion coefficients of PDADMAC during the deposition cycle. Diffusion coefficients were calculated as $D = \frac{q^2 {H_t}^2}{4t}$, , where H_t is the wet thickness of PDADMAC deposited per layer as measured by spectroscopic ellipsometry, q is the normalized mass uptake, and t is adsorption time (see details in Fig. S7 of Supporting Information).

Fig. 3 shows that diffusion of polyacids was dependent on the partner MW and was faster for 8-PMAA than *L*-PMAA in LbL films with all three PDADMACs exposed to 0.2 M NaCl

solutions. The difference in diffusivity between linear and star polyacids was significant (Fig. 3C), suggesting that the small differences in PMAA ionization seen in Fig. 2E cannot explain the observation. Instead, the higher diffusivity is likely attributed to a more compact structure of 8-PMAA star polymers. This result is consistent with our prior result on faster diffusion of more compact star molecules at moderate salt concentrations,[23] although the latter results were obtained using poly[2-(trimethylammonium)ethyl methacrylate chloride] – a polyelectrolyte with twice higher linear charge density (charge per units length) than PDADMAC. Note that in this prior work, the polycation and polyanion unit lengths were matched, and both differences in the polyacid architecture and polyacid ionization contributed to the faster mobility of star polyacids.[23] In contrast, the mismatch between contour length of PMAA and PDADMAC units in this work (Figs. 2F&S2) minimized the effect of molecular architecture on ionization, enabling decoupling of the effect of molecular compactness on polymer diffusion.

Fig. 3C shows that the diffusion coefficients (plotted using the power law dependence commonly used for polymer diffusion as a function of molecular weight) decreased with an increment in partner MWs for both linear and star architectures, but the trend of change was different for both architectures. For example, $D_{//}$ differed by ~70% for *L*-PMAA* and 8-PMAA* assembled with 35 kDa PDADMAC, but as the polycation MW increases to 300 kDa, the difference in $D_{//}$ values minimized for linear and star PMAA*. The data could be successfully fitted with the power law dependences, but the power exponent for both linear and star PMAA* in Fig. 3C were significantly below both sticky reptation and Rouse predictions.[25] Specifically, the power exponent of $D_{//}$ *vs*. PDADMAC MW dependence increased from -0.22±0.01 for linear PMAA to -0.53±0.02 for star PMAA. To interpret these dependencies, one should note that the MW of PMAA was not varied in these experiments. Instead, changes in MW of PDADMAC impact PMAA

diffusion through its effect on film layering and molecular conformations which determine the diffusion path of the polymer. Specifically, due to maximization of entropy through the formation of loops during adsorption of higher-MW polyelectrolytes,[31,32] both the bilayer thickness[33,34] and internal roughness (*i.e.* intermixing)[18] of LbL films can increase with polyelectrolyte MW for non-linearly grown films with relatively sparse polymer-polymer ionic pairing. The two-fold difference in the slope in Fig. 3C for *L*-PMAA and 8-PMAA can be attributed to the difference in the size of the hopping sites between linear and star PMAA as determined previously.[23] The larger polymer segments involved in the diffusion of star PMAA[23] decrease the probability of finding a new ionic pairing, potentially leading to a stronger effect of PDADMAC MW on the diffusion of star PMAA within the films. Finally, the differences in the film layering between star and linear PMAA can also contribute to the differences in the dependencies of $D_{//}$ on the polycation MW. Stronger molecular intermixing in star-containing films was indirectly suggested in several prior publications,[10,11,35-37] and directly demonstrated in our recent work by employing neutron reflectometry measurements.[23] The stronger spreading of PMAA stars and PDADMAC chains within the film, together with the different underlying mechanisms of diffusion of the star polyacids *via* the mechanism of arm retraction[38] and lower anisotropy of star-containing multilayers[23] can all collectively contribute to the still weak, but stronger than for linear PMAA chains, dependence of star PMAA molecules on the MW of the polycation partner.

Overall, the weak dependence of diffusion of PMAA chains on PDADMAC MW suggests that it is unlikely that PMAA diffuses together with the polycation chains being bound within a PMAA/PDADMAC complex, but instead PMAA moves individually in the landscape of obstacles determined by the ionic pairing within the multilayer film. This result differs from the observation of PSS diffusion in PSS/PDADMAC films, where a strong power dependence of PSS on

PDADMAC MW was observed,[19] highlighting the important roles of polyanion type and charge density on its diffusion within the multilayers. While in the PSS/PDADMAC system the linear charge densities in the polycation and the polyanion are mismatched (*i.e*. the charge-to-charge distance in PDADMAC chain is twice larger than in PSS or fully ionized PMAA), the charge density in PMAA can be controlled by pH and reduced in acidic conditions (such as at pH 5 used in our experiments). Perhaps even more importantly, carboxylate ions are known to form weaker ionic pairing with polycations,[24] favoring decoupling of PMAA mobility from the polycation partner molecules.

While FRAP experiments followed only the diffusion of *L*-PMAA* or 8-PMAA*, we were also able to evaluate the diffusivity of unlabeled PDADMAC. To that end, we monitored adsorption of PDADMAC on preassembled LbL films using *in-situ* ellipsometry as detailed in the caption of Fig. 3, Supporting Information and Fig. S7. **Fig. 3D** shows that the diffusion coefficients of the polycation for both *L*-PMAA/PDADMAC and 8-PMAA/PDADMAC systems decreased with the increase of PDADMAC molecular weight, but the scaling laws differed for all-linear and star-containing films, following $D \sim M_w^{-0.98\pm0.22}$ and $D \sim M_w^{-0.69\pm0.01}$ dependences, respectively. The power exponents of these dependences were much lower than the prediction for the diffusion of unentangled chains using the sticky Rouse model[25] and slightly lower than the values for the PSS diffusion in a matrix of relatively low MW PDADMAC reported by Helm and co-workers.[19] An interesting observation from Fig. 3D is a weaker effect of PMAA architecture on the polycation molecular diffusivity. Comparison of Fig. 3C&D also shows that the scaling dependences for diffusion of poly(carboxylic acid)s and the polycations as a function of polycation MW are drastically different. This further supports the concept of relatively independent diffusion of the polycation and linear or star weak polyacids in their assemblies.

SUPPORTING INFORMATION

Refer to the Supporting Information for detailed descriptions of the materials and methods used in this manuscript, and figures for PMAA and PDADMAC component ratios within the LbL films, schematics for charge mismatch between PDADMAC and PMAA units, the kinetics of thickness loss from PMAA/PDADMAC films upon exposure to 0.2 M NaCl, example deconvolutions of carboxyl peaks from the infrared spectrum of *L*-PMAA/PDADMAC films, swelling on PMAA/PDADMAC films in 0 M and 0.2 M NaCl conditions, FCS data for Alexa-488, labeled *L*-PMAA and labeled 8-PMAA in solution, and *in situ* measurements of PDADMAC adsorption for the calculation of vertical PDADMAC diffusion coefficients.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Conceptualization, A.A., S.A.S.; synthesis, A.A.; investigation, P.S., J.B.; writing—original draft preparation, J.B., P.S., A.A., S.A.S.; writing—review and editing, J.B., P.S., A.A., S.A.S.;

funding acquisition, S.A.S. All authors have read and agreed to the published version of the manuscript.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its Supporting Information.

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